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Original Spec., Claims, Drawing and Abstract
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Description

Process for Producing Crystalline 1,2-Polybutadiene

Technical Field

The present invention relates to a process for producing crystalline 1,2-polybutadiene, and more particularly to a process for producing 1,2-polybutadiene having a high crystallinity using a specific catalyst system, wherein the vinyl bond content of a polymer obtained is high, and the molecular weight thereof is adjustable.

Background Art

1,2-Polybutadiene having crystallinity has hitherto been obtained by a catalyst comprising a phosphine complex of a cobalt salt, a trialkylaluminum and water (patent document 1: JP-B-44-32425, patent document 2: JP-A-1-249788), a catalyst comprising a phosphine complex of a cobalt salt and methylaluminoxane (patent document 3: JP-A-8-59733), or a catalyst comprising a cobalt salt slurry, a phosphine solution and methylaluminoxane [non-patent document 1: Dilip C. D. Nath, Takeshi Shiono and Tomiki Ikeda, *Journal of Polymer Science*, Vol. 40, 3086-3092 (2002)].

In the catalyst systems described these, it can be known by analogy that a phosphine compound having three aromatic groups is substantially necessary in the production of a 1,2-polybutadiene-based polymer having a crystallinity of 34%

or more. However, when those phosphine compounds are used, it is required to lower the polymerization temperature, which causes an increase in the amount of a solvent used for preventing precipitation, and in the production of the 1,2-polybutadiene-based polymer obtained by an exothermic reaction, the problem of increasing energy loss such as the necessity for higher cooling capacity to a polymerization reactor.

In the above-mentioned patent document 1 (JP-B4432425), there is described an example to use diphenylethylphosphine as a phosphine compound having one aliphatic group and two aromatic groups. However, it is described that an amorphous (that is to say, having a crystallinity of 0%) polymer is obtained when the phosphine compound is used. It is difficult to know the production of a 1,2-polybutadiene-based polymer having a crystallinity of 34% or more by analogy with the category of phosphines as specifically exemplified in the gazette concerned, that is to say, the phosphine compound having one aliphatic group and two aromatic groups.

Further, in the catalyst systems described in these, when the phosphine complex of the cobalt salt is used, equipment for preparing a catalyst component becomes large to necessitate excessive investment, because of low solubility of the phosphine complex in an organic solvent. Furthermore, when a cobalt chloride slurry is used, the efficiency of catalyst is low. It is therefore necessary to use a large amount of catalyst in order to obtain a polymer, which causes the problems of the coloration of the polymer due to residual catalyst and the like.

The present invention relates to a process for producing 1,2-polybutadiene having a high crystallinity using a specific catalyst system, wherein the vinyl bond content of a polymer obtained is high, and the molecular weight thereof is adjustable.

Further, the present invention relates to a process for producing crystalline 1,2-polybutadiene having a high crystallinity, wherein the vinyl bond content of a polymer obtained is high, and the molecular weight thereof is adjustable, using a specific catalyst system which can be prepared as a high concentration catalyst component and provide the polymer by a small amount of catalyst, by using a catalyst system in which an active halogen-containing compound is added, in addition to a cobalt salt, a phosphine compound and an organic aluminum compound.

Disclosure of the Invention

The present invention relates to a process for producing crystalline 1,2-polybutadiene, which is characterized in that 1,3-butadiene is polymerized in a hydrocarbon solvent using a catalyst system comprising (A) a cobalt salt, (B1) a phosphine compound having one branched aliphatic group of 3 or more carbon atoms or one alicyclic group of 5 or more carbon atoms and two aromatic groups, and (C) an organic aluminum compound (hereinafter also referred to as "production process 1").

Further, the present invention relates to a process for producing crystalline 1,2-polybutadiene, which is

characterized in that 1,3-butadiene is polymerized in a hydrocarbon solvent using a catalyst system comprising (A) a cobalt salt, (B) (B1) a phosphine compound having one branched aliphatic group of 3 or more carbon atoms or one alicyclic group of 5 or more carbon atoms and two aromatic groups and/or (B2) a phosphine compound having three aromatic groups, (C) an organic aluminum compound and (D) an active halogen-containing compound (hereinafter also referred to as "production process 2", and production process 1 and production process 2 are also referred to as generally as "the present invention" or "the production process of the present invention").

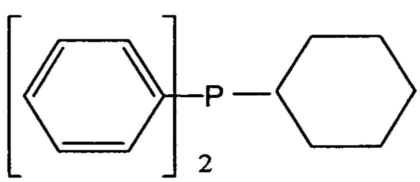
Brief Description of the Drawing

Fig. 1 is a flow chart showing a preferred production process for obtaining crystalline 1,2-polybutadiene of the present invention.

Best Mode for Carrying Out the Invention

(A) The cobalt salt used in the catalyst of the present invention is a cobalt salt of an organic acid such as cobalt chloride, cobalt bromide, cobalt iodide, cobalt octylate, cobalt versatate or cobalt naphthenate, or the like, and a cobalt salt of an organic acid such as cobalt octylate, cobalt versatate or cobalt naphthenate is preferred in that no halogen atom is contained. Further, of these, cobalt octylate, cobalt versatate or cobalt naphthenate is preferred from the point of high solubility in an organic solvent.

Further, as (B1) the above-mentioned phosphine compound having one branched aliphatic group of 3 or more carbon atoms or one alicyclic group of 5 or more carbon atoms and two aromatic groups, there is preferably used, for example, a phosphine compound having one branched aliphatic group of 3 or more carbon atoms or one alicyclic group of 5 or more carbon atoms and two aromatic groups such as phenyl groups, such as diphenylcyclohexylphosphine shown in formula (1), diphenylisopropylphosphine shown in formula (2), diphenylisobutylphosphine shown in formula (3), diphenyl-t-butylphosphine shown in formula (4), diphenylcyclopentylphosphine shown in formula (5), diphenyl(4-methylcyclohexyl)phosphine shown in formula (6), diphenylcycloheptylphosphine shown in formula (7) or diphenylcyclooctylphosphine shown in formula (8).



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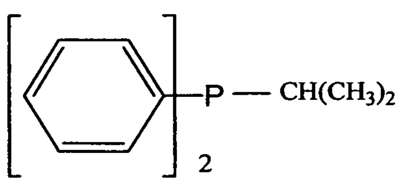

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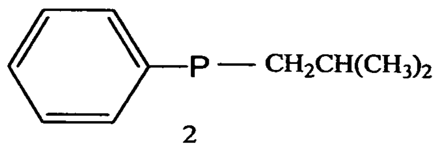

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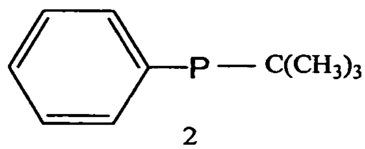

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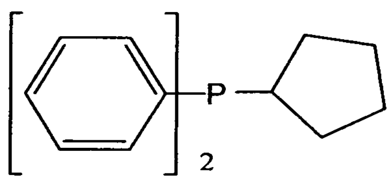

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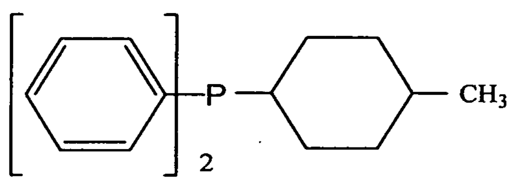

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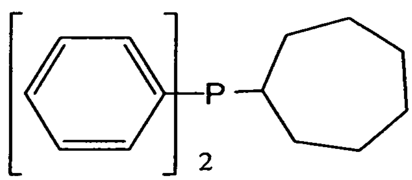

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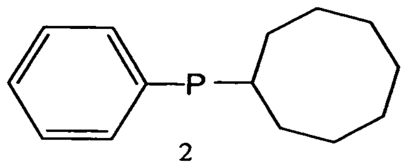

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When this catalyst system comprising (A) the cobalt salt, (B1) the phosphine compound having one branched aliphatic group of 3 or more carbon atoms or one alicyclic group of 5 or more carbon atoms and two aromatic groups and (C) the organic aluminum compound is used, a mixed system of (A) to (C) may be used. However, it is preferred that component (C) is used in combination with a phosphine complex of a cobalt salt comprising component (A) and component (B1). When the phosphine complex of the cobalt salt comprising component (A) and component (B1) is used, there may be used either one previously synthesized, or a method of bringing (A) the cobalt salt into contact with (B1) the phosphine compound having one branched aliphatic group of 3 or more carbon atoms or one alicyclic group of 5 or more carbon atoms and two aromatic groups, in a polymerization system.

Specific examples of the phosphine complexes of the cobalt salts comprising (A) the cobalt salt and (B1) the phosphine compound having one branched aliphatic group of 3 or more carbon atoms or one alicyclic group of 5 or more carbon atoms and two aromatic groups include cobaltbis(diphenyl-cyclohexylphosphine) dichloride, cobaltbis(diphenylcyclo-hexylphosphine) dibromide, cobaltbis(diphenylisopropylphos-

phine) dichloride, cobaltbis(diphenylisopropylphosphine) dibromide, cobaltbis(diphenylisobutylphosphine) dichloride, cobaltbis(diphenylisobutylphosphine) dibromide, cobaltbis-(diphenyl-t-butylphosphine) dichloride, cobaltbis(di-phenyl-t-butylphosphine) dibromide and the like, and preferred are cobaltbis(diphenylcyclohexylphosphine) dichloride and cobaltbis(diphenylcyclohexylphosphine) dibromide.

On the other hand, (B) the phosphine compounds include (B2) a phosphine compound having three aromatic groups (a triarylphosphine) such as triphenylphosphine, tris(3methyl-phenylphosphine), tris(3,5-dimethylphenylphosphine), tris-(4-methoxyphenylphosphine) or tris(3,5-dimethyl, 4-methoxyphenylphosphine), and the like, as well as a diphenyl-alkylphosphine such as the above-mentioned component (B1).

In (B) the phosphine compounds, component (B1) and component (B2) may be used either each alone or both together.

Further, (C) the organic aluminum compounds include methylaluminoxane or a compound obtained by bringing a trialkylaluminum into contact with water.

Of these, as methylaluminoxane, there may be used either one previously synthesized or one synthesized in the polymerization system.

Besides, the above-mentioned trialkylaluminum is trimethylaluminum, triethylaluminum, triisobutylaluminum, trioctylaluminum or the like, and water is used in an amount of 0.2 to 1.0, preferably 0.3 to 0.75, by the molar ratio based on the aluminum atom of the trialkylaluminum.

As for a contacting method of the trialkylaluminum and water, water may be brought into contact with an inert organic solvent solution of the trialkylaluminum, in any state of vapor, liquid and solid (ice). Further, water may be brought into contact, as a dissolved state, a dispersed state or an emulsified state in an inert organic solvent, or as a gas state or a mist state where it exists in an inert gas.

Further, the active halogen-containing compounds, components (D), include, for example, an aluminum halide compound such as a methylaluminum halide such as dimethylaluminum chloride, methylaluminum dichloride, dimethylaluminum bromide, methylaluminum dibromide, dimethylaluminum fluoride or methylaluminum difluoride, or an ethylaluminum halide such as diethylaluminum chloride, ethylaluminum dichloride, diethylaluminum bromide, ethylaluminum dibromide, diethylaluminum fluoride or ethylaluminum difluoride; a boron fluoride complex such as a boron fluoride-phenol complex or a boron fluoride-ether complex; a silane halide compound such as methyltrichlorosilane, dimethylchlorosilane, dimethyldichlorosilane, trimethylchlorosilane or tetrachlorosilane; a metal halide compound such as titanium tetrachloride or tin tetrachloride; an organic active halide such as benzyl chloride, allyl chloride, dibromomethane, dichloroethane or dibromoethane; and the like.

Of these components (D), an aluminum halide compound, a metal halide compound, a silane halide compound and an organic active halide are preferred from the aspect of polymerization

activity.

In the catalyst used in production process 1 of the present invention, the use ratio of (A) the cobalt salt and (B1) the phosphine compound is preferably 1 to 5 mol of (B1) the phosphine compound per mol of (A) the cobalt salt.

Further, the amount of the phosphine complex of the cobalt salt comprising components (A) and (B1) used is within the range of 5,000 to 150,000, preferably 10,000 to 100,000, by the molar ratio of 1,3-butadiene and the cobalt atom in the phosphine complex (1,3-butadiene/Co). When 1,3-butadiene/Co (molar ratio) is less than 5,000, the mechanical strength of a polymer obtained is inferior. On the other hand, exceeding 150,000 results in decreased polymerization activity.

Furthermore, the amount of component (C) (organic aluminum compound) used is within the range of 500 to 4,000, preferably 800 to 2,000, by the molar ratio of 1,3-butadiene and the aluminum atom in component (C) (1,3-butadiene/Al). When 1,3-butadiene/Al (molar ratio) is less than 500, it is economically disadvantageous. On the other hand, exceeding 4,000 results in decreased polymerization activity. The ratio of the aluminum atom of component (C) to the cobalt atom of the phosphine complex of the cobalt salt comprising components (A) and (B1) (Al/Co) is usually from 5 to 300, and preferably about 7.5 to 100. When Al/Co (atomic ratio) is less than 5, polymerization activity is decreased. On the other hand, exceeding 300 results in economical disadvantage.

The catalyst used in production process 1 of the present

invention is prepared by mixing catalyst components in an inert organic solvent in any order. Preferably, as shown in Fig. 1, (A) the cobalt salt is allowed to react with (B1) the phosphine compound in an inert organic solvent to form the phosphine complex of the cobalt salt, then, component (C) is added thereto to prepare the catalyst of the present invention, and 1,3-butadiene is polymerized in a hydrocarbon solvent using this catalyst, thereby obtaining crystalline 1,2-polybutadiene.

On the other hand, in the catalyst used in production process 2 of the present invention, using the cobalt catalyst previously obtained by mixing component (D) and component (A), or component (D), component (A) and component (B) [component (B1) and/or component (B2)], the cobalt catalyst is brought into contact with component (B) and component (C) in the former, or with component (C) in the latter, thereby being able to produce a polymer efficiently.

Alternatively, an aluminum promoter previously obtained by mixing component (C) and component (D) is brought into contact with component (A) and component (B), thereby being able to produce a polymer efficiently.

In the catalyst system used in production process 2 of the present invention, for the use ratio of (A) the cobalt salt, (B) the phosphine compound [component (B1) and/or component (B2)] and (D) the active halogen-containing compound, (B) the phosphine compound is preferably from 0.5 to 5 mol per mol of (A) the cobalt salt. The use ratio of (D) the active

halogen-containing compound is from 0.5 to 10 mol per mol of (A) the cobalt salt.

Further, the amount of (A) the cobalt salt used is within the range of 5,000 to 200,000, preferably 10,000 to 150,000, by the molar ratio of the 1,3-diene and the cobalt atom (1,3-diene/Co). When 1,3-diene/Co (molar ratio) is less than 5,000, the mechanical strength of a polymer obtained is inferior. On the other hand, exceeding 200,000 results in decreased polymerization activity.

Furthermore, the amount of component (C) (aluminoxane) used is within the range of 500 to 4,000, preferably 1000 to 3,000, by the molar ratio of the 1,3-diene and the aluminum atom in component (C) (1,3-diene/Al). When 1,3-diene/Al (molar ratio) is less than 500, it is economically disadvantageous. On the other hand, exceeding 4,000 results in decreased polymerization activity. The ratio of the aluminum atom of component (C) to the cobalt atom of component (A) (Al/Co) is usually from 5 to 300, and preferably from about 7.5 to 100. When Al/Co (atomic ratio) is less than 5, polymerization activity is decreased. On the other hand, exceeding 300 results in economical disadvantage.

As the inert organic solvents used for the preparation of the catalysts in the above-mentioned production processes 1 and 2 of the present invention, there can be used, for example, an aromatic hydrocarbon such as benzene, toluene or xylene, an aliphatic hydrocarbon such as butane, butene, pentane, pentene, hexane, heptane or octane, an alicyclic hydrocarbon such as

cyclopentane or cyclohexane, a chlorinated hydrocarbon such as methylene chloride, 1,2-dichloroethane, 1,1,1-trichloroethane, chlorobenzene, o-dichlorobenzene or p-dichlorobenzene, and a mixture thereof.

As the inert organic solvents used for the preparation of the catalysts, there are also preferably used the same solvents as the polymerization catalysts.

Further, the catalyst may be prepared by previously mixing respective components before it is brought into contact with 1,3-butadiene of the present invention, or can also be prepared by mixing respective components in the presence of a conjugated diene in a polymerization reactor.

In the present invention, 1,2-polybutadiene having a crystallinity of 5% to 40% can be produced by polymerizing 1,3-butadiene in the hydrocarbon solvent using the catalyst system mainly comprising components (A), (B1) and (C), or the catalyst system mainly comprising components (A), (B) [(B1) and/or (B2)], (C) and (D).

In the present invention, a conjugated diene other than 1,3-butadiene can also be used together in an amount of about 10% by weight or less. The conjugated dienes other than 1,3-butadiene, which are used in the present invention, include a 4-alkyl-substituted-1,3-butadiene, a 2-alkyl-substituted-1,3-butadiene and the like. Of these, the 4-alkyl-substituted-1,3-butadienes include 1,3-pentadiene, 1,3-hexadiene, 1,3-heptadiene, 1,3-octadiene, 1,3-nonadiene, 1,3-decadiene and the like. Further, typical examples of the

2-alkyl-substituted1,3-butadienes include 2-methyl-1,3-butadiene (isoprene), 2-ethyl-1,3-butadiene, 2-propyl-1,3-butadiene, 2-isopropyl-1,3-butadiene, 2-butyl-1,3-butadiene, 2-isobutyl-1,3-butadiene, 2-amyl-1,3-butadiene, 2-isoamyl-1,3-butadiene, 2-hexyl-1,3-butadiene, 2-cyclohexyl-1,3-butadiene, 2-isohexyl-1,3-butadiene, 2-heptyl-1,3-butadiene, 2-isoheptyl-1,3-butadiene, 2-octyl-1,3-butadiene, 2-isooctyl-1,3-butadiene and the like. Of these conjugated dienes, preferred examples of the conjugated dienes used as a mixture with 1,3-butadiene include isoprene and 1,3-pentadiene.

The hydrocarbon solvents used as the polymerization solvents include, for example, an aromatic hydrocarbon such as benzene, toluene or xylene, an aliphatic hydrocarbon such as butane, butene, pentane, pentene, hexane, heptane or octane, an alicyclic hydrocarbon such as cyclopentane or cyclohexane, a chlorinated hydrocarbon such as methylene chloride, 1,2-dichloroethane, 1,1,1-trichloroethane, chlorobenzene, o-dichlorobenzene or p-dichlorobenzene, and a mixture thereof. Preferred examples thereof include cyclohexane, heptane, toluene, methylene chloride and the like. More preferred is a non-halogen hydrocarbon solvent such as cyclohexane, heptane or toluene, from the standpoint of the non-halogen series.

The polymerization temperature is usually from -20°C to +120°C, and preferably from +10°C to +90°C. The polymerization reaction may be conducted by either a batch system or a continuous system. The monomer concentration in the solvent

is usually from 5 to 80% by weight, and preferably from 8 to 40% by weight.

Further, in order to produce a polymer, it is necessary that attention is taken to avoid contamination with a compound having inactivating action, such as oxygen, water or carbon dioxide, to the utmost in the polymerization system for preventing inactivation of the catalyst and the polymer of the present invention.

When the polymerization reaction has proceeded to a desired stage, a polymerization terminator such as an alcohol, an antioxidant, an antiaging agent, an ultraviolet ray absorber and the like are added to a reaction mixture, and then, a polymer formed according to an usual method is separated, washed and dried to be able to obtain desired 1,2-polybutadiene.

1,2-Polybutadiene obtained by the production process of the present invention has a vinyl bond content of 85% or more, preferably 90% or more.

Further, the crystallinity of 1,2-polybutadiene obtained by the present invention is preferably from 5 to 40%, and more preferably from 10 to 35%. Less than 5% results in inferior mechanical strength, whereas exceeding 40% results in inferior processability. The crystallinity is adjustable by the polymerization temperature or the like.

Furthermore, the molecular weight of 1,2-polybutadiene obtained by the present invention is usually from 100,000 to 600,000, by the weight average molecular weight in terms of polystyrene. Less than 100,000 results in inferior strength,

whereas exceeding 600,000 results in inferior processability. The molecular weight is adjustable by the aluminum atom/cobalt atom ratio.

The halogen atom content in 1,2-polybutadiene of the present invention thus obtained is preferably low from the standpoint of environmental problems, and is 200 ppm or less, more preferably 100 ppm or less and particularly preferably 50 ppm or less. Exceeding 200 ppm results in an increase in the amount of endocrine disrupter corresponding materials generated in burning in some cases.

Here, the halogen atom content of the resulting polymer can be easily adjusted to 200 ppm or less by using a non-halogen cobalt salt in the catalyst system, particularly in component (B1) or component (B), and by using the above-mentioned non-halogen hydrocarbon solvent as the solvent for catalyst preparation or the polymerization solvent.

Crystalline 1,2-polybutadiene obtained by the present invention is blended as a raw resin or raw rubber, either alone or as a mixture with another synthetic resin, synthetic rubber or natural rubber, further, oil extended with a process oil as needed, and then, ordinary compounding agents for vulcanized rubber such as a filler such as carbon black, a vulcanizing agent and a vulcanization accelerator are added to perform vulcanization as a rubber composition, thereby being able to use for applications requiring mechanical characteristics and wear resistance, for example, tires, hoses, belts, sponges, footwear materials, sheets, films, tubes, packaging materials,

resin modifiers, photosensitive materials and other various industrial goods.

Examples

The present invention will be illustrated in greater detail with reference to the following examples, but the invention should not be construed as being limited by the following examples, as long as it does not exceed a gist thereof.

In the examples, parts and percentages are on a weight basis, unless otherwise specified.

Further, various measurements in the examples were made in accordance with the following methods.

The vinyl bond content (1,2-bond content) of 1,2-polybutadiene was determined by an infrared absorption spectrum method (the Morero's method).

The crystallinity of 1,2-polybutadiene was converted from the density measured by an underwater substitution method, taking the density of 1,2-polybutadiene at a crystallinity of 0% as 0.889 g/cm^3, and the density of 1,2-polybutadiene at a crystallinity of 100% as 0.963 g/cm^3.

The weight average molecular weight (Mw) was measured by gel permeation chromatography (GPC) at 40°C using tetrahydrofuran as a solvent.

The halogen atom content was determined by a fluorescent X-ray measurement (FP method).

The melt flow index (MI) showed the amount (g) of a resin flowed out for a period of time corresponding to 10 minutes under

conditions of a temperature of 150 °C and a load of 2.16 kilograms, with a melt flow indexer.

Example 1

Preparation of Cobaltbis(diphenylcyclohexylphosphine) Dichloride Solution:

In an atmosphere of dry nitrogen, 2.2 g of anhydrous cobalt chloride, 8.0 g of diphenylcyclohexylphosphine and 125 g of methylene chloride were added into a 300- ml pressure bottle, and stirred in a constant temperature water bath of 35°C for 4 hours, followed by separation of a precipitate to obtain an 8% methylene chloride solution of cobaltbis(diphenylcyclohexylphosphine) dichloride. This solution was diluted with methylene chloride, and used as a 0.4% solution.

Polymerization of 1,3-Butadiene:

In an atmosphere of dry nitrogen, 25 g of 1,3-butadiene (BD) and 125 g of cyclohexane were put into a 300- ml pressure bottle, and the 0.4% solution of cobaltbis(diphenylcyclohexylphosphine) dichloride obtained above and a 1% (as Al atoms) solution of methylaluminoxane in toluene were each added so as to give BD/Co (molar ratio) = 30,000 and Al/Co (atomic ratio) = 20, respectively, followed by polymerization in a constant temperature water bath of 50°C for 120 minutes.

Reaction termination was performed by adding a small amount of ethanol as a terminator.

Then, 2,6-di-t-butyl-p-cresol was added in an amount of 0.3 part based on 100 parts of the polymer, and heated on a hot plate to remove the solvents, thereby obtaining the polymer.

The degree of polymerization conversion was determined from the yield. Further, the halogen content in the polymer was measured. The results are shown in Table 1.

Examples 2 to 7

Using the same technique as with Example 1, by cobalt salts and phosphine compounds shown in Table 1, solutions of phosphine complexes of the cobalt salts were prepared, and polymerization of 1,3-butadiene was conducted under conditions of BD/Co ratios and Al/Co ratios shown in Table 1. The results are shown in Table 1.

Comparative Examples 1 to 4

Using the same technique as with Example 1, by cobalt salts and phosphine compounds shown in Table 1, solutions of phosphine complexes of the cobalt salts were prepared, and polymerization of 1,3-butadiene was conducted under conditions of BD/Co ratios and Al/Co ratios shown in Table 1. The results are shown in Table 2.

Table 1

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7
Polymerization Solvent	Cyclo-hexane	Cyclo-hexane	Cyclo-hexane	Cyclo hexane	Cyclo hexane	Cyclo hexane	Cyclo-hexane
Solvent/1,3-Butadiene (Weight Ratio)	5	5	5	5	5	5	5
Cobalt Salt	Cobalt Chloride	Cobalt Chloride	Cobalt Chloride	Cobalt Bromide	Cobalt Chloride	Cobalt Chloride	Cobalt Chloride
Phosphine Compound	Diphenyl cyclo-hexyl-phos-phine	Diphenyl cyclo-hexyl-phos-phine	Diphenyl cyclo hexyl-phos-phine	Diphenyl cyclo-hexyl-phos-phine	Diphenyl-iso-propyl-phosphine	Diphenyl-isobutyl-phosphine	Diphenyl-t-butyl-phos-phine
Polymerization Temperature	50°C	50°C	50°C	50°C	50°C	50°C	50°C
Polymerization Time	120 min	120 min	120 min	120 min	120 min	120 min	120 min
BD/Co (Molar Ratio)	30,000	45,000	60,000	90,000	45,000	60,000	60,000
Al/Co (Atomic Ratio)	20	30	40	60	30	40	40
Degree of Polymerization Conversion	82%	80%	80%	81%	81%	82%	78%
State of Solution	Uniform	Uniform	Uniform	Uniform	Uniform	Uniform	Uniform
Vinyl Bond Content	95%	95%	95%	94%	94%	91%	92%
Crystallinity	37%	37%	37%	36%	36%	34%	34%
Weight Average Molecular Weight	150,000	170,000	230,000	140,000	160,000	180,000	170,000
Halogen Content	45 ppm	36 ppm	27 ppm	40 ppm	35 ppm	28 ppm	30 ppm

Table 2

	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
Polymerization Solvent	Cyclo hexane	Cyclo hexane	Cyclo hexane	Cyclo hexane
Solvent/1,3-Butadiene (Weight Ratio)	5	5	5	5
Cobalt Salt	Cobalt Chloride	Cobalt Chloride	Cobalt Bromide	Cobalt Bromide
Phosphine Compound	Tris(3,5-dimethylphenyl)-phosphine	Tris(3,5-dimethylphenyl)-phosphine	Tris(3,5-dimethylphenyl)-phosphine	Tris(3,5-dimethylphenyl)-phosphine
Polymerization Temperature	50°C	30°C	50°C	30°C
Polymerization Time	120 min	180 min	120 min	180 min
BD/Co (Molar Ratio)	60,000	60,000	90,000	90,000
Al/Co (Atomic Ratio)	40	40	60	60
Degree of Polymerization Conversion	80%	78%	81%	79%
State of Solution	Uniform	Precipitated	Uniform	Precipitated
Vinyl Bond Content	92%	94%	92%	94%
Crystallinity	25%	35%	24%	35%
Weight Average Molecular Weight	190,000	220,000	210,000	250,000
Halogen Content	28 ppm	28 ppm	39 ppm	42 ppm

As apparent from Tables 1 and 2, it turns out that the polymers having a high crystallinity can be obtained at a polymerization temperature of 50°C in Examples 1 to 7, but that the polymerization temperature must be lowered to 30°C in Comparative Examples 1 to 4, in order to obtain an equivalent crystallinity. Consequently, Examples 1 to 7 require a shorter polymerization time, but Comparative Examples 2 and 4 require a longer polymerization time, which practically causes a problem.

Example 8

Preparation of Phosphine Complex Solution:

Using the same technique as with Example 1, by a cobalt salt and a phosphine compound shown in Table 3, a solution of a phosphine complex of the cobalt salt was prepared.

Polymerization of 1,3-Butadiene:

In an atmosphere of dry nitrogen, 25 g of 1,3-butadiene (BD) and 250 g of methylene chloride were put into a 300-ml pressure bottle, and water in the system was adjusted to water/Al (molar ratio) = 0.7. In a state cooled to 10°C, an 8% solution of triisobutylaluminum in methylene chloride was added so as to give BD/Co (molar ratio) = 20,000 and Al/Co (atomic ratio) = 20, followed by thorough stirring. Then, the resulting solution of the phosphine complex of the cobalt salt was added so as to give BD/Co (molar ratio) = 20,000, and thereafter, the bottle was immediately placed in a constant temperature water bath of 20°C, followed by polymerization for 60 minutes.

Reaction termination was performed by adding a small amount of ethanol as a terminator. Then, 2,6-di-t-butylp-cresol was added in an amount of 0.3 part based on 100 parts of the polymer, and heated on a hot plate to remove the solvents, thereby obtaining the polymer. The degree of polymerization conversion was determined from the yield. The results are shown in Table 3.

Comparative Examples 5 to 7

Using the same technique as with Example 8, by cobalt salts and phosphine compounds shown in Table 2, solutions of phosphine complexes of the cobalt salts were prepared, and

polymerization of 1,3-butadiene was conducted under conditions of BD/Co ratios and Al/Co ratios shown in Table 3. The results are shown in Table 3.

Table 3

	Example 8	Comparative Example 5	Comparative Example 6	Comparative Example 7
Polymerization Solvent	Methylene Chloride	Methylene Chloride	Methylene Chloride	Methylene Chloride
Solvent/1,3-Butadiene (Weight Ratio)	10	10	10	10
Cobalt Salt	Cobalt Bromide	Cobalt Bromide	Cobalt Bromide	Cobalt Bromide
Phosphine Compound	Diphenylcyclohexyl phosphine	Tris(3,5-dimethylphenyl)-phosphine	Tris(3,5-dimethylphenyl)-phosphine	Tris(3,5-dimethoxyphenyl)-phosphine
Polymerization Temperature	20°C	20°C	-5°C	20°C
Polymerization Time	60 min	60 min	90 min	60 min
BD/Co (Molar Ratio)	20,000	20,000	15,000	20,000
Al/Co (Atomic Ratio)	20	20	15	20
Degree of Polymerization Conversion	86%	81%	83%	84%
State of Solution	Uniform	Uniform	Precipitated	Uniform
Vinyl Bond Content	95%	92%	95%	93%
Crystallinity	38%	29%	37%	30%
Weight Average Molecular Weight	160,000	170,000	180,000	160,000
Halogen Content	351 ppm	387 ppm	524 ppm	483 ppm

As apparent from Table 3, it turns out that the polymer having a high crystallinity has been obtained at a polymerization temperature of 20°C in Example 8, but that the polymers having a low crystallinity have been obtained at a polymerization temperature of 20°C in Comparative Examples 5 and 7. On the other hand, it turns out that the polymerization temperature must be lowered to -5°C in Comparative Example 6,

in order to obtain an equivalent crystallinity. Consequently, Example 8 requires a shorter polymerization time, but Comparative Example 6 requires a longer polymerization time, which practically causes a problem.

As described above, in a method which can be known by analogy from the descriptions of JP-B4432425, JP-A-1-249788 and JP-A-8-59733, that is to say, in a case that a phosphine compound having three aromatic groups is used as the phosphine compound, a lower crystallinity is obtained under equivalent conditions. When it is intended to obtain a polymer having an equivalent crystallinity, the polymerization temperature must be lowered, which causes an increase in the amount of a solvent used for preventing precipitation, and in the production of the 1,2-polybutadiene obtained by an exothermic reaction, the problem of increasing energy loss such as the necessity for higher cooling capacity to a polymerization reactor. It is therefore apparent that the method is industrially disadvantageous.

Example 9

Preparation of Catalyst Solution:

In an atmosphere of dry nitrogen, 2 ml of toluene, 0.25 ml of a 0.1 mol/liter toluene solution of (A) cobalt octylate, 0.31 ml of a 0.1 mol/liter toluene solution of (B2) tris(3-methylphenylphosphine) and 0.1 mol/liter toluene solution of (D) dimethylaluminum chloride were added into a 30-ml pressure bottle, and stirred at room temperature for 10 minutes. Then, 2.95 ml of a 1% (as Al atoms) toluene solution

of (C) methylaluminoxane was added thereto, followed by further stirring for 10 minutes to prepare a cobalt catalyst solution.

Polymerization of 1,3-Butadiene

In an atmosphere of dry nitrogen, 60 ml of 1,3-butadiene (BD) and 248 ml of cyclohexane were put into a 500-ml pressure bottle, and 0.70 ml of the resulting cobalt catalyst solution was added, followed by polymerization in a constant temperature water bath of 36°C for 60 minutes.

Reaction termination was performed by adding a small amount of ethanol as a terminator.

Then, 2,6-di-t-butyl-p-cresol was added in an amount of 0.3 part based on 100 parts of the polymer, and heated on a hot plate to remove the solvents, thereby obtaining the polymer. The degree of polymerization conversion was determined from the yield. The ratios of respective catalyst components and butadiene and the results of polymerization are shown in Table 4.

Examples 10 to 15

Using the same technique as with Example 9, by use of a cobalt salt, a phosphine compound and an active halide shown in Table 4, cobalt catalyst solutions were prepared, and polymerization of 1,3-butadiene was conducted under conditions of the amount of the cobalt salt, the amount of the phosphine compound and the amount of the active halide shown in Table 4. The results are shown in Table 4.

Comparative Examples 8 and 9

Using the same technique as with Example 9, solutions were

similarly prepared without adding any one of the cobalt salt, the phosphine compound and the active halide shown in Table 5, and polymerization of butadiene was attempted. The results are shown in Table 5.

The absence of an active halide brought about extremely low polymerization activity, unfavorably resulting in not only high industrial production cost, but also increased residual cobalt. Further, the absence of a phosphine failed to obtain 1,2-polybutadiene.

As apparent from Tables 4 and 5, the polymers having a high crystallinity could be obtained at a polymerization temperature of 36°C in a high yield in Examples 9 to 13, but polymerization scarcely proceeded to obtain the polymers only in a low yield, in Comparative Examples 8 and 9.

Examples 16 to 18

Experiments were made by changing the kind of active halogen compound, and the results thereof are shown in Table 5.

As apparent from Table 5, crystalline 1,2-polybutadiene was obtained in a good yield, even when an active halide such as a silane halide compound or titanium tetrachloride was used. The results are shown in Table 5.

Example 19

Polymerization was conducted in the same manner as with Example 9 with the exception that 60 ml of butadiene was replaced by 54 ml of butadiene and 7 ml of isoprene. In the polymer formed, 7.1% of isoprene was copolymerized.

The polymer had a melting point of 87°C, and was a crystalline butadiene-isoprene copolymer. The results are shown in Table 5.

Table 4

	Example						
	9	10	11	12	13	14	15
Catalyst							
(A) Cobalt Salt (mmol) Cobalt Octylate Cobalt Naphthenate	0.0057	0.0057	0.0057	0.006	0.006	0.0057	0.0057
(B) Phosphine Compound (mmol) Tris(3-methylphenylphosphine) Diphenylcyclohexylphosphine	0.009	0.0071	0.0043	0.009	0.012	0.009	0.009
(D) Active Halogen Compound (mmol) Dimethylaluminum Chloride Dimethylchlorosilane Trimethylchlorosilane Titanium Tetrachloride	0.011	0.014	0.0086	0.012	0.012	0.011	0.011
(C) Aluminoxane (mmol) Methylaluminoxane	0.23	0.23	0.23	0.23	0.23	0.23	0.23
Solvent for Catalyst Preparation	Toluene	Toluene	Toluene	Methychlo	Methychlo	Toluene	Toluene
Polymerization Conditions							
Monomer	BD	BD	BD	BD	BD	BD	BD
Polymerization Solvent	CHX	CHX	CHX	CHX	CHX	CHX	CHX
Polymerization Temperature	36°C	36°C	36°C	36°C	36°C	36°C	50°C
Polymerization Time (min)	60	60	60	60	60	60	60
Results of Polymerization							
Degree of Conversion (%)	53	56	40	68	64	51	65
Vinyl Bond Content (%)	93	93	93	93	93	93	95
Crystallinity (%)	28	28	28	28	28	28	35
Weight Average Molecular Weight (10,000)	26.6	28.4	28.2	27.8	28.9	26.6	28.4
MI (g/10 min)	1.04	1.23	0.17	5.2	4.3	0.98	0.65

Table 5

	Example				Comparative Example	
	16	17	18	19	8	9
Catalyst						
(A) Cobalt Salt (mmol)						
Cobalt Octylate	0.0057	0.006		0.0057	0.006	0.006
Cobalt Naphthenate			0.006			
(B) Phosphine Compound (mmol)						
Tris(3-methylphenylphosphine)	0.009	0.009	0.009		0	0.012
Diphenylcyclohexylphosphine				0.009		
(D) Active Halogen Compound (mmol)						
Dimethylaluminum Chloride				0.011	0.012	0
Dimethylchlorosilane	0.011					
Trimethylchlorosilane		0.011				
Titanium Tetrachloride			0.011			
(C) Aluminoxane (mmol)						
Methylaluminoxane	0.23	0.23	0.23	0.23	0.23	0.23
Solvent for Catalyst Preparation	Toluene	Toluene	Toluene	Toluene	Toluene	Toluene
Polymerization Conditions						
Monomer	BD	BD	BD	BD/IP	BD	BD
Polymerization Solvent	CHX	CHX	CHX	CHX	CHX	CHX
Polymerization Temperature	36°C	36°C	36°C	36°C	36°C	36°C
Polymerization Time (min)	60	60	60	60	60	60
Results of Polymerization						
Degree of Conversion (%)	55	50	45	35	6	9
Vinyl Bond Content (%)	93	93	93			
Crystallinity (%)	28	28	28	Melting point 87 °C	-	27
Weight Average Molecular Weight (10,000)	28.2	27.8	28.9	18.8	-	34.9
MI (g/10 min)	0.68	0.75	0.58	5.7	-	0.15

Abbreviations: Methychlo = methylene chloride, BD = butadiene, IP = isoprene, CHX = cyclohexane

As described above, cobalt octylate used in the present invention is a compound high in solubility, which is soluble in toluene at any ratio. On the other hand, the solubility of a cobalt bromide-tris(3-methylphenylphosphine) complex [$CoBr_2 \cdot 2P(m\text{-}CH_3C_5H_4)_3$] in toluene is as little as 0.4%, so that a large amount of solvent is required. Accordingly, a large adjusting tank is required for industrial use. Compared to the method using the complex shown in JP-B-44-32425 or JP-A-1-249788, the present invention can use the cobalt catalyst having a high concentration, which makes efficient production possible.

Further, compared to the method using cobalt chloride in the slurry state, which is shown in *Journal of Polymer Science*, Vol. 40, 3086-3092 (2002), in the present invention, the cobalt amount is as little as about 1/3, and the aluminoxane amount is as little as about 1/10. This shows that the catalysts are efficiently utilized.

Industrial Applicability

Crystalline 1,2-polybutadiene obtained by the present invention is blended as a raw resin or raw rubber, either alone or as a mixture with another synthetic resin, synthetic rubber or natural rubber, further, oil extended with a process oil as needed, and then, ordinary compounding agents for vulcanized rubber such as a filler such as carbon black, a vulcanizing agent

and a vulcanization accelerator are added to perform vulcanization as a rubber composition, thereby being able to use for applications requiring mechanical characteristics and wear resistance, for example, tires, hoses, belts, sponges, footwear materials, sheets, films, tubes, packaging materials, resin modifiers, photosensitive materials and other various industrial goods.

Claims

1. A process for producing crystalline 1,2-polybutadiene, which is characterized in that 1,3-butadiene is polymerized in a hydrocarbon solvent using a catalyst system comprising (A) a cobalt salt, (B1) a phosphine compound having one branched aliphatic group of 3 or more carbon atoms or one alicyclic group of 5 or more carbon atoms and two aromatic groups, and (C) an organic aluminum compound.

2. The process for producing crystalline 1,2-polybutadiene according to claim 1, wherein the catalyst system comprises a phosphine complex of a cobalt salt obtained by mixing component (A) and component (B1), and component (C).

3. The process for producing crystalline 1,2-polybutadiene according to claim 1 or 2, wherein component (A) is at least one selected from the group consisting of cobalt chloride, cobalt bromide, cobalt octylate, cobalt versatate and cobalt naphthenate.

4. The process for producing crystalline 1,2-polybutadiene according to claim 1 or 2, wherein component (B1) is diphenylcyclohexylphosphine.

5. The process for producing crystalline 1,2-polybutadiene according to any one of claims 1 to 4, wherein the use ratio of component (B1) to mol of component (A) is from 1 to 5 mol.

6. The process for producing crystalline 1,2-polybutadiene according to any one of claims 1 to 5, wherein the amount of component (C) used is within the range of 500 to 4,000

by the molar ratio of 1,3-butadiene and the aluminum atom in component (C) (1,3-butadiene/Al).

7. The process for producing crystalline 1,2-polybutadiene according to any one of claims 1 to 7, wherein the hydrocarbon solvent is cyclohexane and/or methylene chloride.

8. The process for producing crystalline 1,2-polybutadiene according to any one of claims 1 to 7, wherein the polymerization temperature is from -20°C to +120°C.

9. The process for producing crystalline 1,2-polybutadiene according to any one of claims 1 to 8, wherein the crystallinity of the resulting 1,2-polybutadiene is from 5 to 40%.

10. A process for producing crystalline 1,2-polybutadiene, which is characterized in that 1,3-butadiene is polymerized in a hydrocarbon solvent using a catalyst system comprising (A) a cobalt salt, (B) (B1) a phosphine compound having one branched aliphatic group of 3 or more carbon atoms or one alicyclic group of 5 or more carbon atoms and two aromatic groups and/or (B2) a phosphine compound having three aromatic groups, (C) an organic aluminum compound and (D) an active halogen-containing compound.

11. The process for producing crystalline 1,2-polybutadiene according to claim 10, wherein a cobalt catalyst previously obtained by mixing component (D) and component (A), or component (D), component (A) and component (B) is used as the catalyst system

12. The process for producing crystalline 1,2-poly-

butadiene according to claim 10, wherein a promoter previously obtained by mixing component (C) and component (D) is used as the catalyst system.

13. The process for producing crystalline 1,2-polybutadiene according to any one of claims 10 to 12, wherein the use ratio of component (B) to mol of component (A) is from 0.5 to 5 mol, and the use ratio of component (D) to mol of component (A) is from 0.5 to 10 mol.

14. The process for producing crystalline 1,2-polybutadiene according to any one of claims 10 to 13, wherein component (A) is at least one selected from the group consisting of cobalt acetate, cobalt lactate, cobalt octylate, cobalt octanoate, cobalt stearate, cobalt versatate and cobalt naphthenate.

15. The process for producing crystalline 1,2-polybutadiene according to any one of claims 10 to 14, wherein compound (D) is at least one selected from the group consisting of an aluminum halide compound, a metal halide compound, a silane halide compound and an organic active halide.

16. The process for producing crystalline 1,2-polybutadiene according to any one of claims 10 to 15, wherein the hydrocarbon solvent is at least one selected from the group consisting of cyclohexane, hexane and methylene chloride.

17. The process for producing crystalline 1,2-polybutadiene according to any one of claims 10 to 16, wherein the polymerization temperature is from -20°C to +120°C.

18. The process for producing crystalline 1,2-poly-

butadiene according to any one of claims 10 to 17, wherein the crystallinity of the resulting 1,2-polybutadiene is from 5 to 40%.